

Comparison of the Interactions of Aminopyralid vs. Clopyralid with Soil

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Laboratory studies were conducted to compare the soil adsorption of aminopyralid and clopyralid with the use of batch-slurry and centrifugation assays. The calculated soil binding constants for both herbicides varied between the two techniques, but the centrifugation assay had a lower coefficient of variation compared to the batch-slurry assay. These results indicate that a centrifugation assay is a more accurate procedure for measuring the interaction of aminopyralid and clopyralid with soils. Aminopyralid adsorbed more tightly than clopyralid to six of the eight soils tested. Adsorption K_d values ranged from 0.083 to 0.364 for clopyralid and 0.106 to 0.697 for aminopyralid. Pearson correlation analysis indicated that binding of both herbicides was highly correlated to soil organic matter and texture but not to soil pH. On average, soil thin-layer chromatography indicated that aminopyralid was less mobile ($R_f = 0.82$) than clopyralid ($R_f = 0.91$), although both were mobile. These results suggest that aminopyralid will have a lower leaching potential than clopyralid. Lower potential aminopyralid soil leaching, coupled with low use rates, suggests it may be the herbicide of choice in areas where potential for leaching could be a concern.

Nomenclature: Aminopyralid; clopyralid.

Key words: Soil adsorption, K_d , R_f .

Aminopyralid and clopyralid are pyridine carboxylic acid herbicides that control a wide spectrum of broadleaf weeds in the Asteraceae, Fabaceae, and Solanaceae families through foliar and soil applications. Although clopyralid has been used for many years, aminopyralid is a relatively new herbicide for use on rangelands, pastures, natural areas, noncroplands, right-of-ways, and riparian areas (Carrithers et al. 2005). Aminopyralid has rapidly become a new herbicide of choice for control of many invasive perennial weeds because of its spectrum of weed control, low use rate, and high level of efficacy. Enloe et al. (2007) reported that aminopyralid provides the same or better weed control compared to clopyralid but at lower rates even though aminopyralid is absorbed and translocated less than clopyralid in Canada thistle (*Cirsium arvense* L.) (Bukun et al. 2009).

There is an abundance of information on the environmental fate of clopyralid, but very little has been published on aminopyralid. A comparison of the physical and chemical properties of both herbicides is shown in Table 1. Both herbicides are acidic, with relatively low pK_a s. Aminopyralid is slightly less hydrophilic than clopyralid. Reported soil binding ratio (K_d) values for clopyralid range from 0.01 to 0.10 (Pik et al. 1977; Tomlin 1994) and an average K_{oc} (the soil binding ratio divided by the fraction of soil organic matter) of 6. Aminopyralid appears to adsorb more tightly to soils based on the reported K_{oc} (10.8) although soil binding of both herbicides is low. The reported half-lives in soils are similar (Senseman et al. 2007).

Adsorption is one of most important factors affecting the fate of pesticides in soils. Herbicide availability in soil can affect its degradation rate, plant availability, and efficacy (Kah and Brown 2007). The relationships between K_d , soil organic matter (OM) and pH are also important values for pesticide fate models to predict herbicide behavior among varying soil characteristics (Farenhorst et al. 2003, 2008; Novak et al. 1997).

The low K_d and relatively long half-life of clopyralid in the soil would suggest that this herbicide has a high leaching potential (Pik et al. 1977; Smith and Aubin 1989). Sakaliene et al. (2009) reported that clopyralid was more mobile than dicamba, mecoprop, and pendimethalin in a field lysimeter study, although less than 3% of the applied herbicides leached from the lysimeter. Other field studies have also shown that although clopyralid can leach; it generally stays in the top 30 cm of the soil profile (Bergstrom et al. 1991; Bovey and Richardson 1991; Elliott et al. 2000). There are no papers yet on the leachability of aminopyralid.

There are multiple methods to determine herbicide binding to soil. The most common method is the batch-slurry technique, where soil is treated with a large volume of water, usually in a 1:1 or higher ratio of soil weight to water volume. Soil adsorption guidelines advise that such studies should be conducted at a soil-to-solution ratio that achieves between 30 and 50% adsorption (OECD 1997). The problem with this procedure for herbicides that do not bind tightly to the soil, such as clopyralid and aminopyralid, is that the lowest practical ratio for batch-slurry techniques is 1:1. An alternative method is a centrifugation method to determine adsorption coefficient of organic compounds (Walker and Jurado-Exposito 1998). This method depends on treating soil at field capacity and centrifuging out the plant available water. Kah and Brown (2007) proposed that this method provides adequate results to determine pesticide leaching potential and is advantageous for pesticide with very low adsorption coefficient, because it yields satisfactory adsorption level and reduces variability.

Another method to determine the relative mobility of herbicides in different soils utilizes a soil thin-layer plate (TLC) technique developed by Helling and Turner (1968). Helling (1971) used the R_f values (the ratio of the distance traveled by the solute front to that of the solvent front) on a standard soil, to classify pesticide soil mobility. Johnson and Sims (1998) reported negative correlation between R_f values and soil organic matter content for atrazine in different soil types.

Clopyralid exhibits low soil adsorption and high water solubility. Aminopyralid's chemical structure and properties are similar to those of clopyralid, but there are limited data published on aminopyralid soil adsorption and mobility. The

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Table 1. Physical and chemical characteristics of clopyralid and aminopyralid (Senseman et al. 2007).

Herbicide	Molecular weight	pK _a	Water solubility	Log K _{ow}	K _{oc}	Soil half-life
	g mole ⁻¹		g L ⁻¹		ml g ⁻¹	d
Clopyralid	292	2.3	1	-1.81 (pH 5)	6	12 to 70
Aminopyralid	207	2.56	2.5	-1.76 (pH 5)	10.8	25 to 35

objectives of this study were (1) to compare the difference between the batch-slurry method versus the centrifugation method on calculating clopyralid and aminopyralid K_d ; (2) to compare the relationship between the effect of soil texture, pH, and OM on the binding of aminopyralid and clopyralid, and (3) to determine the relationship between soil properties and the relative mobility of clopyralid and aminopyralid.

Materials and Methods

Soils. Soils were collected from various locations throughout the United States, air dried, sieved through a 2-mm sieve, and maintained in the dark at 4 °C until use. The physical characteristics and names of the soils are shown in Table 2. Soil textures and properties were determined by Harris Laboratory, Kansas City, KS.

Batch-Slurry K_d Assay. Two grams of soil were weighed into 15-ml test tubes equipped with Teflon-lined lids.¹ An equilibration solution was prepared by diluting 50 µl of 1 mg ml⁻¹ stock solutions of either aminopyralid² or clopyralid to 100 ml with water. Radioactive labeled aminopyralid (specific activity 9.03×10^5 kBq mmol⁻¹) or clopyralid (specific activity 1.103×10^6 kBq mmol⁻¹) was also added to the application solutions at a level of 4.25×10^2 kBq ml⁻¹. Four milliliters of the equilibration solution were added to each 2 g of soil. Final soil concentrations were equivalent to 1 mg kg⁻¹ of soil and contained 0.17 kBq ¹⁴C. The samples were shaken for 24 hr, then centrifuged at $1,500 \times g$ for 30 min. The concentration of compound not absorbed by the soil was determined by counting 1 ml of the resulting supernatant by liquid scintillation spectroscopy (LSS).³ Each soil–herbicide combination was replicated three times and the experiment was repeated.

The concentration of herbicide remaining in the soil was calculated with the equation

$$C_s = v(C_i - C_w) / S_{wt}, \quad [1]$$

where v (ml) is the volume of the added water in suspension; S_{wt} is the soil weight (g), C_i is the initial concentration of herbicide in the water phase (mg l⁻¹); C_w is the final

concentration of the herbicide in the water phase (mg l⁻¹); and C_s is the concentration of herbicide adsorbed to the soil (mg g⁻¹). The soil adsorption coefficient K_d (ml g⁻¹) was calculated with the equation

$$K_d = C_s / C_w. \quad [2]$$

The K_{oc} was calculated with the equation:

$$K_{oc} = K_d / f_{oc}, \quad [3]$$

where f_{oc} is the fraction of soil organic carbon.

Centrifugation K_d Assay. The level of herbicide contained in plant available water was determined using a centrifuge tube technique (Kah and Brown 2007). The field capacity of each soil used in the experiment was determined by the pressure-plate technique (Klute 1986). One hundred grams of soil (dry weight) were fortified with aminopyralid or clopyralid at concentration of 1 µg g⁻¹ of soil and spiked with radiolabelled compound at a level of 4.25×10^2 kBq g⁻¹. Water was added to bring each soil to field capacity and the soil was allowed to equilibrate for 24 h. After 24 h moisture content was determined by drying a sample at 105 °C and determining the weight before and after drying. Soils were gently mixed and 15 g of each soil sample was placed in an insert which had a filter on the bottom.⁴ The insert was placed in a 50-ml tube and centrifuged at $1,500 \times g$ for 1 hr. Following centrifugation the water collected in the centrifuge tube was transferred to a vial and the volume of plant-available water was determined by weighing the amount of water collected in the centrifuge tube. The amount of radioactivity in the extracted water was determined by LSS. Each soil–herbicide combination was replicated four times and the experiment was repeated.

The K_d of the herbicides was calculated from the centrifugation assay using the procedure of Kah and Brown (2007). The equation was

$$C_s = [C_i - (vC_e)] / S_{wt}, \quad [4]$$

where C_s is the concentration of herbicide adsorbed to the soil (mg g⁻¹); v is the volume of water centrifuged from the soil (ml); C_i is the total amount of herbicide applied to the system (g); C_e is the concentration of herbicide in the centrifuged water (g ml⁻¹) and S_{wt} is the dry weight of the soil (g). The K_d was calculated as described previously.

Thin-Layer Plate Chromatography (TLC). Soil slurries for the eight soils described in Table 1 were prepared and a 1-mm layer uniformly applied on 20- by 20-cm glass plates and allowed to dry. Application solutions were prepared by adding

Table 2. Physical characteristics of eight soils.

Location	Soil series	Taxonomy	pH	Organic matter	Sand	Silt	Clay
					%		
Michigan	Spinks loamy sand	Sandy, mixed, mesic Lamellic Hapludalfs	5.9	1.2	81	11	8
Colorado	Julesburg sandy loam	Fine-loamy, mixed, superactive, mesic Aridic Argiustolls	7.2	1.4	90	4	6
North Carolina	Gilead sandy loam	Fine, kaolinitic, thermic Aquic Hapludults	5.2	1.6	90	3	7
California	Imperial silty clay	Fine, smectitic, calcareous, hyperthermic Vertic Torrifluvents	8	2	32	23	45
Colorado	Weld silt loam	Fine, smectitic, mesic Aridic Argiustolls	6.1	2.5	26	51	23
Idaho	Thatuna silt loam	Fine-silty, mixed, superactive, mesic Oxyaquic Argixerolls	5.8	3.1	13	59	28
Illinois	Drummer silty clay loam	Fine-silty, mixed, superactive, mesic Typic Endoaquolls	5.4	5.9	16	48	36
Minnesota	Webster clay loam	Fine-loamy, mixed, superactive, mesic Typic Endoaquolls	6.9	7.9	36	30	34

Table 3. Soil binding (K_d) of clopyralid and aminopyralid to eight soils.^a

Soil	OM	Clopyralid			Aminopyralid		
		K_d			K_d		
		Batch	Centrifugation	K_{oc}	Batch	Centrifugation	K_{oc}
		kg L ⁻¹					
	%						
Spinks loamy sand	1.2	0.089 c	0.084 d	12.1	0.148 de	0.106 e	15.2
Julesburg sandy loam	1.4	0.078 c	0.083 d	10.2	0.071 e	0.107 e	13.2
Gilead sandy loam	1.6	0.178 b	0.083 d	8.9	0.427 c	0.179 de	19.3
Imperial silty clay	2	0.003 c	0.152 c	13.1	0.071 e	0.163 de	14.1
Weld silt loam	2.5	0.196 b	0.168 c	11.6	0.245 d	0.188 de	13.0
Thatuna silt loam	3.1	0.184 b	0.247 b	13.7	0.628 b	0.391 c	21.7
Drummer silty clay loam	5.9	0.323 a	0.364 a	10.6	0.866 a	0.561 b	16.4
Webster clay loam	7.9	0.206 b	0.303 ab	6.6	0.769 a	0.697 a	15.2

^a OM, soil organic matter; K_{oc} , soil binding ratio based on soil organic matter; Means followed by same letter within each column are equivalent according to Tukey's adjustment at the 0.05 level.

4.2 kBq to 500 μ l of a 1 mg ml⁻¹ stock solution of each compound. The TLC plate was spotted with 25 μ l of application solution as a 2.5-cm-wide band, and the plate was developed by placing it vertically in a glass chromatography chamber containing deionized water. The plate was removed when the water reached approximately two-thirds of the length of the plates and allowed to dry. After drying the plates were exposed to x-ray film⁵ for 1 wk. A mobility factor (R_f) was determined by calculating the ratio of the distance traveled by the compound to that of the solvent front. Each herbicide-soil combination had three replicates and experiments were repeated.

Data Analysis. Data from all experiments were subjected to Levene's test for homogeneity of variance to determine if data from repeat experiments could be pooled (SAS Institute 2004). The binding of clopyralid and aminopyralid to the soil (K_d) and mobility on soil TLC plates was subjected to ANOVA.⁶ Treatment means were separated at the 5% level of significance with the use of the Tukey test. Pearson's correlation⁶ was performed between herbicide, soil organic matter content (OM), pH, silt, clay and K_d values ($P \leq 0.05$). A paired t -test⁶ was conducted on the data where required.

Results and Discussion

Comparison between Batch Slurry and Centrifugation.

There were no significant differences ($P < 0.05$) between repeated experiments according to Levene's test for homogeneity of variance so all data were pooled. There were differences between the calculated K_d from the batch-slurry technique versus the centrifugation assay for several soils (Table 3). This difference was particularly evident with the

Gilead sandy loam, Imperial silty clay, Tathuna silt loam, and Webster clay loam for both clopyralid and aminopyralid. The batch-slurry technique indicated very little binding of either herbicide to the Imperial silty clay ($K_d = 0.003$ to 0.071), whereas the centrifugation assay showed significant binding for both herbicides ($K_d = 0.152$ to 0.163). In other soils (Thatuna silt loam and Webster clay loam) the K_d for clopyralid was significantly higher using the centrifugation method compared to the batch-slurry method, but just the opposite was true for aminopyralid (Table 3). Kah and Brown (2007) reported similar variability on differences between these two methods depending on the herbicide and the soil.

Another difference between the batch-slurry assay and the centrifugation assay was the variability among replications. Each experiment had three replications for each herbicide-soil combination. The average coefficient of variation (CV) for the batch-slurry assay among all the soils was 144 and 17 (data not shown) for clopyralid and aminopyralid, respectively, whereas the average CV for the centrifugation assay was 5 and 4 (data not shown) for clopyralid and aminopyralid, respectively. These results suggest that there was greater variation in the batch-slurry assay compared to the centrifugation assay for these two herbicides that are not bound tightly to soil. These results support the conclusions of Walker and Jurado-Exposito (1998) and Kah and Brown (2007) that the centrifugation assay is a good technique for estimating binding of herbicides with very low affinity for soil. The rest of our analyses are based on the K_d values calculated from the centrifugation assay.

Clopyralid adsorbed less tightly to all eight soils compared to aminopyralid (Table 3). The calculated K_{oc} values agree with those published for clopyralid and aminopyralid (Senseman et al. 2007), which reported that aminopyralid adsorbs more tightly to soil than clopyralid. The greater adsorption of aminopyralid to these soils compared to clopyralid could be due to multiple factors. Aminopyralid is slightly more lipophilic than clopyralid so it may interact more strongly with OM. In addition, the amino substitution on the pyridine ring may interact more strongly with either the soil surfaces or with divalent cations in the soil, forming a bridge between the herbicide and the soil colloidal surface. More research is needed to determine the exact mechanism of adsorption of these herbicides to soil.

Soil-Properties Effect on K_d . There were significant correlations between K_d for both herbicides and OM, clay, silt, and sand across the eight soils (Tables 4 and 5). Because

Table 4. Pearson's correlation between clopyralid binding (K_d) and soil properties.

	OM ^a	pH	Sand	Silt	Clay
K_d	0.891***	-0.18	-0.78***	0.706***	0.694***
OM		-0.0567	-0.555**	0.447*	0.575***
pH			0.00584	-0.246	0.349
Sand				-0.933***	-0.848***
Silt					0.601***

^a OM, soil organic matter.

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.001$.

Table 5. Pearson's correlation between aminopyralid binding (K_d) and soil properties.

	OM ^a	pH	Sand	Silt	Clay
K_d	0.975***	-0.171	-0.596**	0.516**	0.566**
OM		-0.0567	-0.555**	0.447*	0.575**
pH			0.00584	-0.246	0.349
Sand				-0.933***	-0.848***
Silt					0.601**

^a OM, soil organic matter.

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.001$.

OM, clay, silt, and sand were highly correlated with each other, we could not separate soil texture from OM. However, there was no significant correlation between soil pH and herbicide adsorption for either herbicide. These results are different from those of Cox et al. (1995) who found that soil pH and OM explained the adsorption of clopyralid in three soils from Canada. It is somewhat surprising that there was no correlation between soil pH and the adsorption of clopyralid and aminopyralid to these soils. Both herbicides are highly acidic with low pK_a s (2.3 to 2.56). In the pH range of the soils used in this research (5.2 to 8.0), more than 99% of both of these herbicides would be in the anionic form.

Thin-Layer Plate Chromatography (TLC). Data from repeated experiments were combined on the basis of Levene's homogeneity of variance ($P < 0.05$). Aminopyralid moved less than clopyralid in the Spinks loamy sand, Imperial silty clay, Weld silt loam, Thatuna silt loam, Drummer silty clay loam, and Webster clay loam but there was no significant difference in the Julesburg sandy loam, and Gilead sandy loam (Table 6). The lack of difference between the two herbicides in the Julesburg sandy loam and Gilead sandy loam is probably due to the fact that neither herbicide adsorbs tightly to these soils (Table 3). As the K_d of the herbicide increased the R_f value decreased for both compounds (Figure 1). The correlation between K_d and R_f was statistically significant ($P < 0.01$) for aminopyralid. The correlation between K_d and R_f for clopyralid was significant at $P = 0.076$. These correlations are not unexpected, because the adsorption of an herbicide to the soil plays a major role in how much the herbicide will move. These results suggest that aminopyralid will have a lower leaching potential than

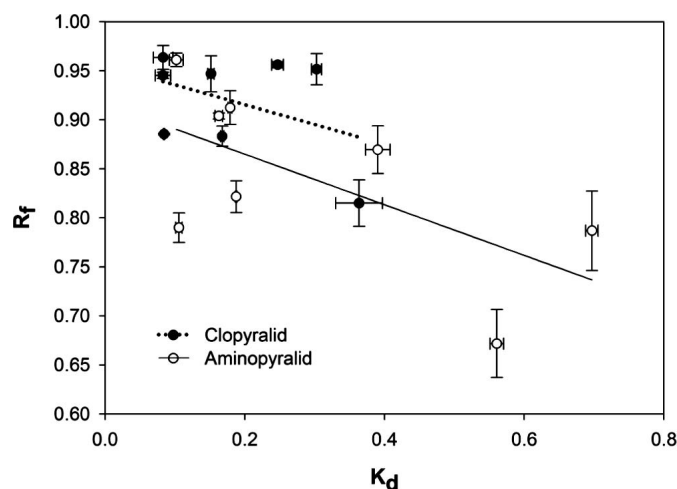


Figure 1. Relationship between herbicide soil binding (K_d) and relative movement (R_f) on soil thin layer plates in eight soils. Regression equations: clopyralid (solid line) $R_f = 0.954 - 0.191 K_d$ ($P = 0.076$; $R^2 = 0.14$); aminopyralid (dashed line): $R_f = 0.917 - 0.260 K_d$ ($P = 0.002$; $R^2 = 0.35$).

clopyralid. However, both herbicides were highly mobile in the soils tested.

These data indicate that aminopyralid adsorbs more tightly to soils compared to clopyralid. Organic matter appeared to be the primary soil component that determined the binding of these two herbicides to the soils tested. Neither herbicide adsorbed tightly to any of the soils tested. A groundwater ubiquity score (GUS) (Gustafson 1989) was calculated for both herbicides based on the average K_{oc} in these eight soils and the reported half-lives from Senseman et al. (2007). The GUS for clopyralid ranged from 3.2 to 5.5, whereas the GUS for aminopyralid was from 3.9 to 4.1. These GUS scores would suggest that both herbicides have a potential to leach. However, field research with clopyralid has shown that the herbicide stays within the top 30 cm of the soil profile (Bergström et al. 1991; Bovey and Richardson 1991; Elliott et al. 2000). In addition, aminopyralid is used at approximately one-third of the rate of clopyralid and is degraded more rapidly. At present, aminopyralid is only labeled for use in noncropland where intensive irrigation is not likely. These factors would suggest that aminopyralid should also stay within the upper soil profile, because it adsorbs more tightly to soil and moved less in soil thin-layer plates compared to clopyralid, and should not leach under normal field conditions.

Table 6. Movement of clopyralid and aminopyralid on soil thin-layer plates.

Soil	R_f^a	
	Clopyralid ^b	Aminopyralid
Spinks loamy sand	0.88* ^c b	0.79 b
Julesburg sandy loam	0.96 a	0.96 a
Gilead sandy loam	0.94* b	0.87 bc
Imperial silty clay	0.95* cd	0.88 bc
Weld silt loam	0.88* cd	0.82 c
Thatuna silt loam	0.92 de	0.87 d
Drummer silty clay loam	0.82* e	0.67 d
Webster clay loam	0.95* e	0.73 d

^a R_f , ratio of the distance the herbicide moved and the distance of the water front.

^b Means followed by same letter within each column are equivalent according to Tukey's adjustment at the 0.05 level.

^c Asterisks indicate a significant difference between clopyralid and aminopyralid ($P < 0.05$).

Sources of Materials

- Corning Inc., Corning, NY 14831.
- Dow AgroSciences LLC, Indianapolis, IN 46268.
- Packard Tri-Carb (Model 2500 TR), Packard Instrument Co., Meriden, CT 06450.
- Whatman VectraSpin 20, Whatman International Ltd., England.
- Kodak X-Ray Film, Eastman Kodak Co., Rochester, NY 14650.
- Systat Software, Inc., San Jose, CA 95440.

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